



Enhanced Bioremediation Using Sulfate and/or Nitrate

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Environmental Technology

Remediation Management Technology Meeting

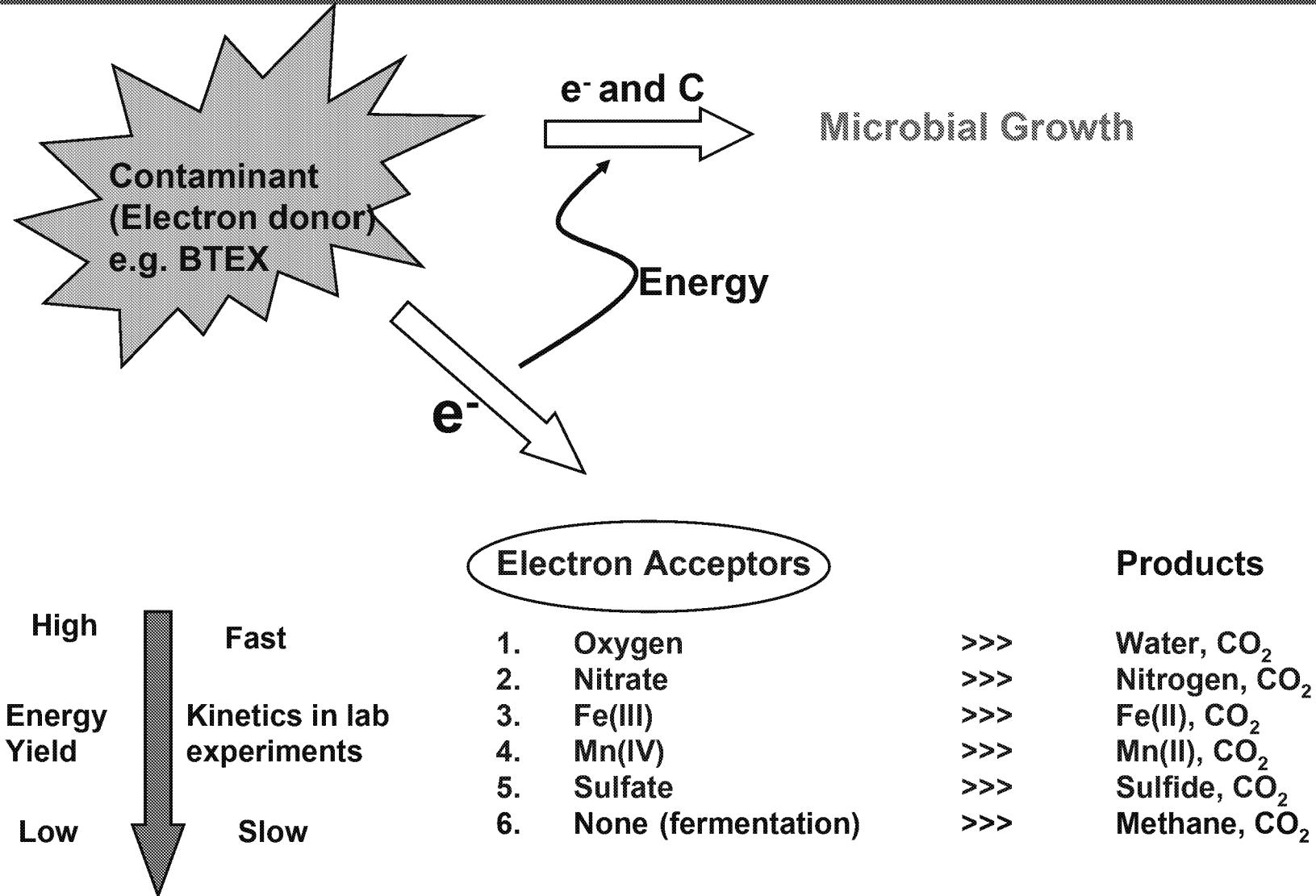
Warrenville

January 22, 2004

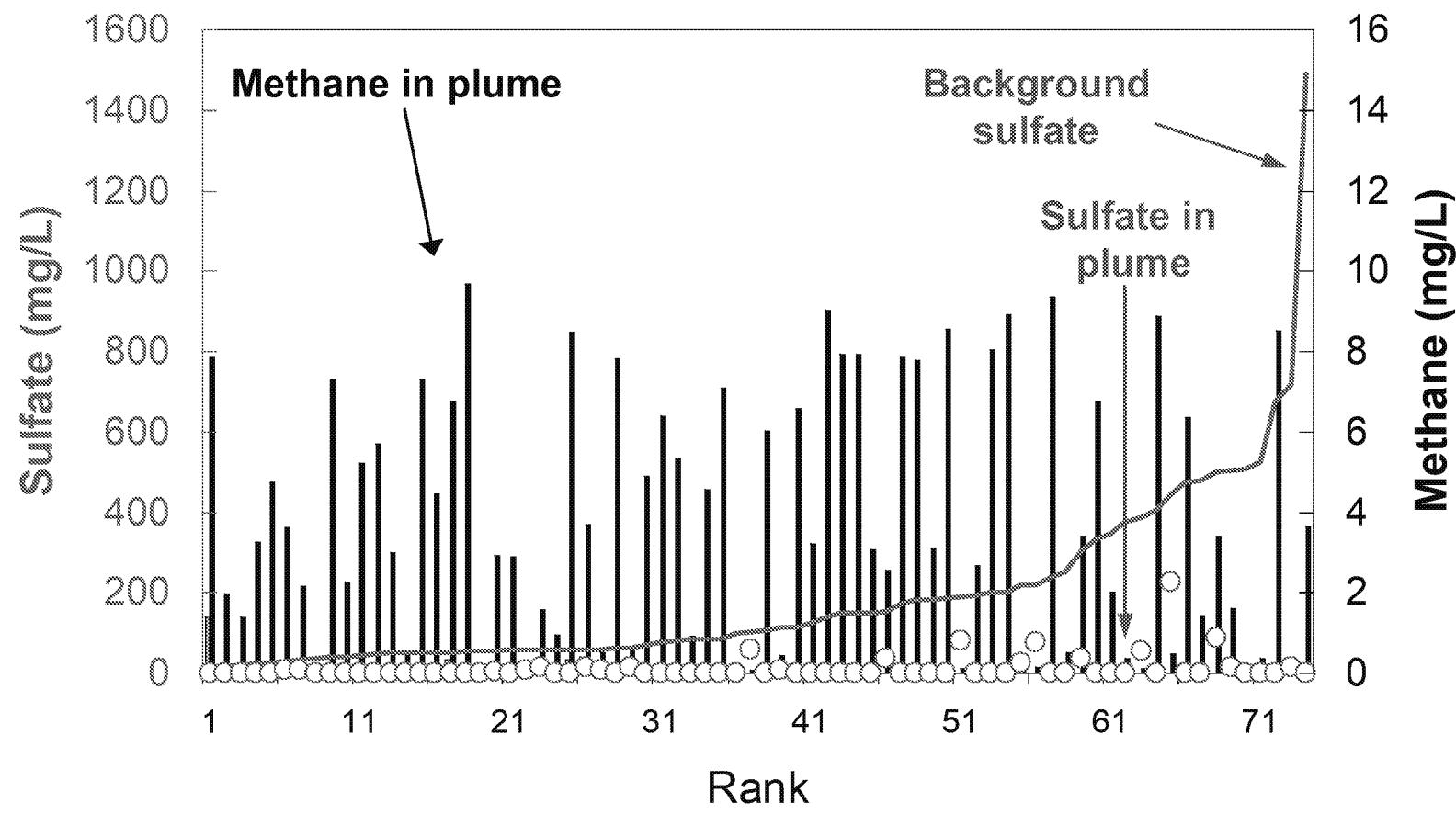
Overview

- Why add sulfate (and/or nitrate)?
- **What kinds of contaminants can be addressed?**
- Why bother if anaerobic rates are slower than aerobic rates?
- What about Hydrogen Sulfide?
- Application Guidance

Hydrocarbon Biodegradation



Sulfate in Ground Water at Retail Sites(BP-EPA Study)



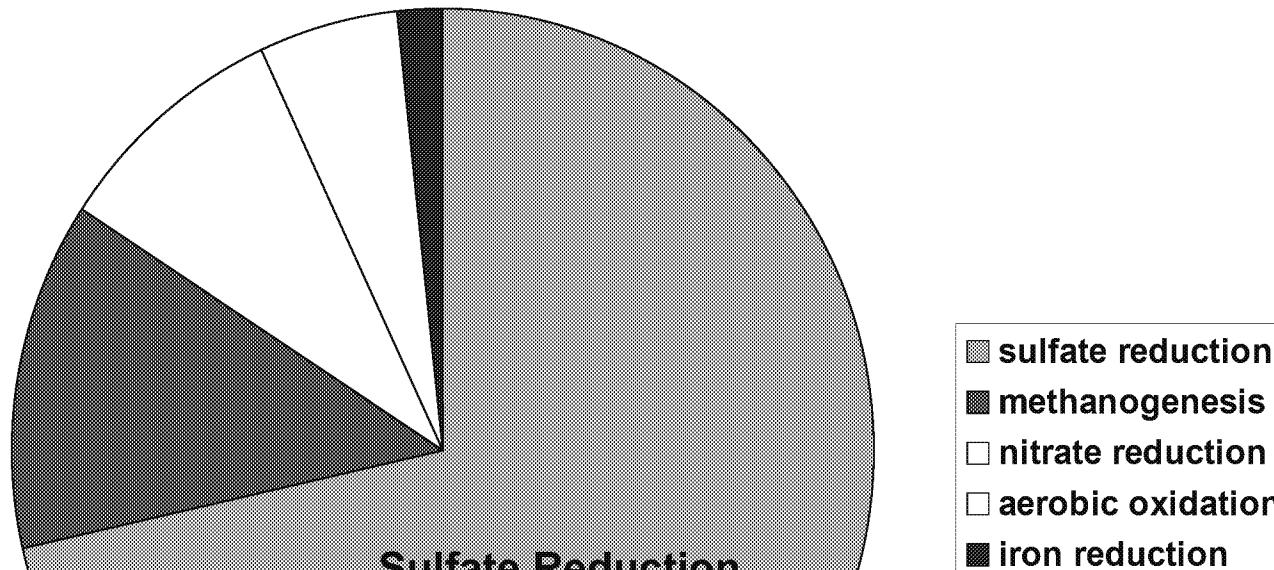
Sulfate is absent in most of the plumes

Why Sulfate?



| Electron Acceptor (EA) | Maximum Concentration (mg/L) | Mass of benzene degraded per unit mass of EA | Potential Benzene Degraded (mg/L) | Issues |
|------------------------|------------------------------|--|-----------------------------------|---|
| Oxygen (in air) | 9 - 10 | 0.33 | 3.0 – 3.3 | <ul style="list-style-type: none">Limited solubilityNumerous oxygen sinksPotential aquifer cloggingBiofouling near injection point |
| Pure Oxygen | 60 - 70 | 0.33 | 19.8 – 23.1 | |
| Sulfate | 100 – 250* | 0.22 | 22.0 – 55.0 | <ul style="list-style-type: none">Hydrogen sulfide; never documented as an issue in the fieldSecondary MCL for sulfate – 250 mg/L* |
| Nitrate | 80 - 100 | 0.21 | 16.8 – 21.0 | <ul style="list-style-type: none">DW concernPrimary MCL – 10 mg/L NO₃-N (45 mg/L NO₃) |
| Iron (III) | 0 - 1 | 0.024 | 0 – 0.024 | <ul style="list-style-type: none">Very low solubilityAquifer clogging |

Sulfate Does the Heavy Lifting!



Gasoline Release Sites

Based on median consumptions of
electron acceptors at 74 sites

BP-EPA study

Field Data – Conclusions



- Most hydrocarbon plumes are anaerobic and depleted of sulfate
- Sulfate reduction is important in ground water

⇒ Adding sulfate to ground water will likely stimulate BTEX degradation

- No solubility constraints (unlike oxygen)
- No chemical sinks (unlike oxygen)
- Can address “non-target” electron acceptor demand enabling contaminants of concern (e.g. benzene) to “see” oxygen

Is Anaerobic Biodegradation Slower?



- **Laboratory Experiments**
 - Electron acceptor supply (DO, nitrate,...) >> Electron Donor (BTEX) demand
 - Rate dictated by biodegradation
 - A > NR > IR > SR > M (rates follow same order)
- **Natural Field Setting**
 - Electron donor demand (BTEX) >> Electron acceptor supply (DO, nitrate,...)
 - Rate dictated by transport of electron acceptors
 - A ~ NR ~ IR ~ SR (rates are similar)
 - M (rate dictated by biodegradation)

No, rates are comparable in the field

Data from Push-pull Tests

| Environment | Method | First order rate constant (day ⁻¹) | Reference |
|------------------------------------|---------------------|--|------------------------|
| Sulfate Reduction | | | |
| Petroleum Impacted Aquifer (PIA) | Flow path | 0.02 to 0.08 | Chappelle, 1996 |
| PIA | Augmented flow path | 0.1 | Cunningham et al. 2000 |
| Petroleum and CHC impacted aquifer | Push-pull tests | 4.32 to 6.48 | McGuire et al., 2002 |
| Nitrate Reduction | | | |
| PIA | Push-pull tests | 5.28 | Schroth et al., 1998 |
| PIA | Augmented flow path | 0.1 to 0.6 | Cunningham et al. 2000 |
| Petroleum and CHC impacted aquifer | Push-pull tests | 5.04 to 7.44 | McGuire et al., 2002 |

Normal Alkanes



Table 2 Evidence for anaerobic alkane biodegradation

| Electron acceptor | Type of culture | Alkanes degraded | Reference |
|-------------------|--------------------|---|----------------------------------|
| Denitrification | Pure, strain OcN1 | C8 | Ehrenreich <i>et al.</i> , 2000 |
| | Pure, strain HdN1 | C16 | |
| Denitrification | Pure, strain HxN1 | C6 | Rabus <i>et al.</i> , 2001 |
| Denitrification | Enrichment | Pristane (2,6,10,14-tetramethylpentadecane) | Bregnard <i>et al.</i> , 1997 |
| Sulfate reducing | Pure, strain Hxd3 | C12–C20 | Aeckersberg <i>et al.</i> , 1991 |
| Sulfate reducing | Pure, strain Pnd3 | C14–C17 | Aeckersberg <i>et al.</i> , 1998 |
| Sulfate reducing | Pure, strain AK-01 | C13–C18 | So and Young, 1999a and b |
| Sulfate reducing | Enrichment | C12 | Kropp <i>et al.</i> , 2000 |
| Sulfate reducing | Enrichment | C15–C34 | Caldwell <i>et al.</i> , 1998 |
| Methanogenic | Enrichment | C16 | Anderson and Lovley 2000 |
| Methanogenic | Enrichment | C16 | Zengler <i>et al.</i> , 1999 |

Normal Alkanes

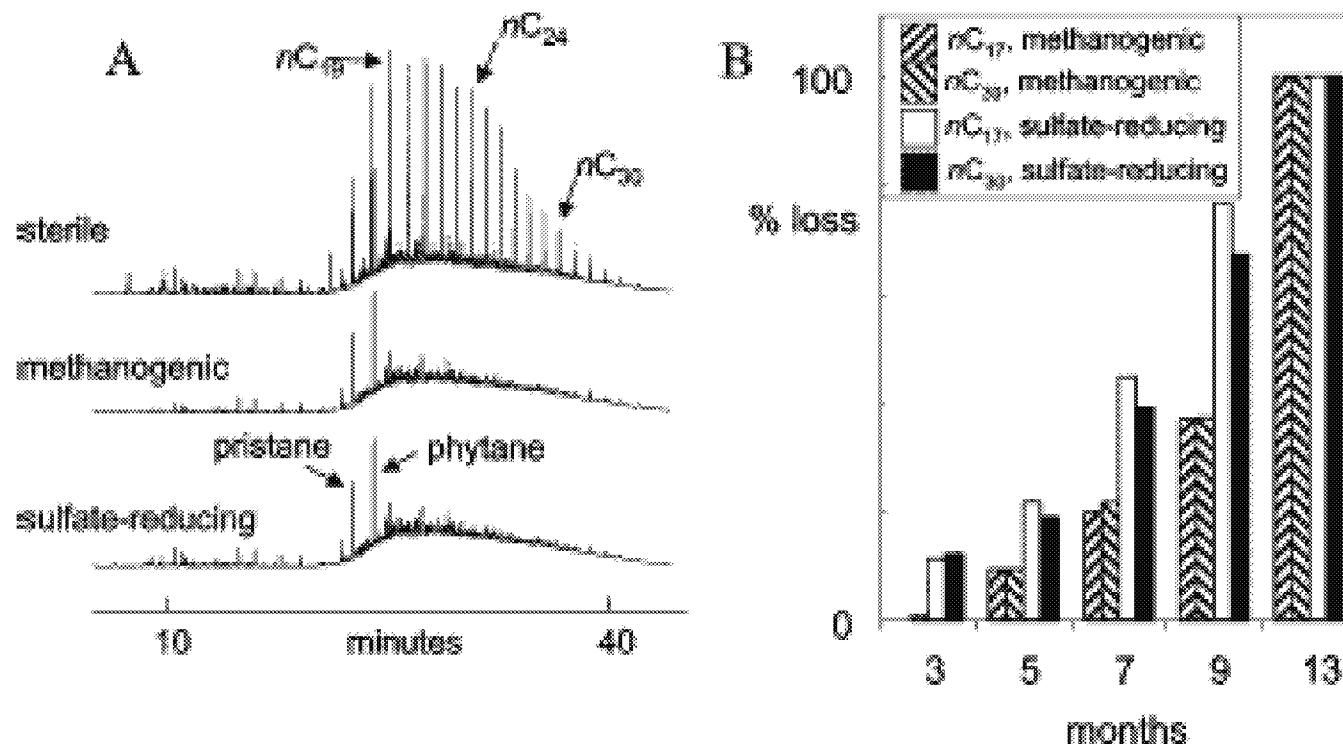


FIGURE 3. *n*-Alkane biodegradation in artificially weathered Alaska North Slope crude oil. (A) Chromatograms of residual oil after 13 months of incubation. (B) Time course of biodegradation of two *n*-alkanes. The incubations initially contained 3.62 mg of heptadecane and 1.13 mg of triacontane.

PAH

Table 1 Evidence for anaerobic polycyclic aromatic hydrocarbon (PAH) degradation

| Electron acceptor | Culture* | PAH compounds degraded | Reference |
|-----------------------|----------|--|------------------------------------|
| Denitrification** | PC | anthracene, phenanthrene, pyrene | McNally et al., 1998 |
| Denitrification* | PC | naphthalene | Rockne et al., 2000 |
| Denitrification | EC | acenaphthalene, naphthalene | Mihelcic and Luthy 1988 |
| Denitrification | EC | naphthalene, phenanthrene | Rockne and Strand 2001 and 1998 |
| Sulfate reducing | PC | naphthalene | Galushko et al., 1999 |
| Sulfate reducing | EC | naphthalene | Bedessem et al., 1997 |
| Sulfate reducing | EC | naphthalene, phenanthrene, fluorene, fluoranthene | Coates et al., 1997 |
| Sulfate reducing | EC | naphthalene, phenanthrene | Zhang and Young 1997 |
| Sulfate reducing | EC | naphthalene, phenanthrene | Rockne and Strand 1998 |
| Sulfate reducing | EC | naphthalene, phenanthrene | Hayes et al., 1999 |
| Sulfate reducing | EC | 2-methylnaphthalene | Annweiler et al., 2000 |
| Sulfate reducing | EC | naphthalene | Meckenstock et al., 2001 |
| Manganese reducing | EC | naphthalene | Langerhoff et al., 1996 |

*culture EC = enrichment culture; PC = pure culture; *nitrate reduced to nitrite; **nitrate reduced to nitrous oxide

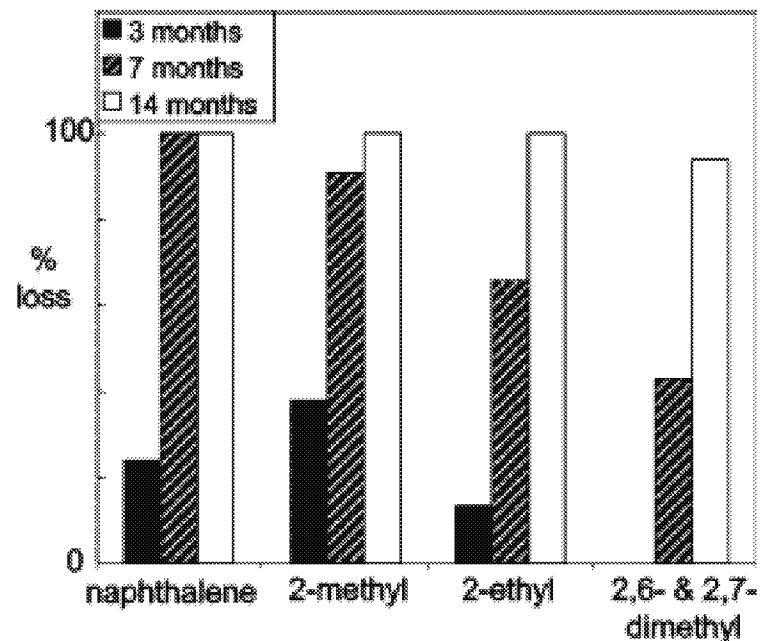


FIGURE 6. Time course of naphthalene homologue biodegradation in Alba crude oil.

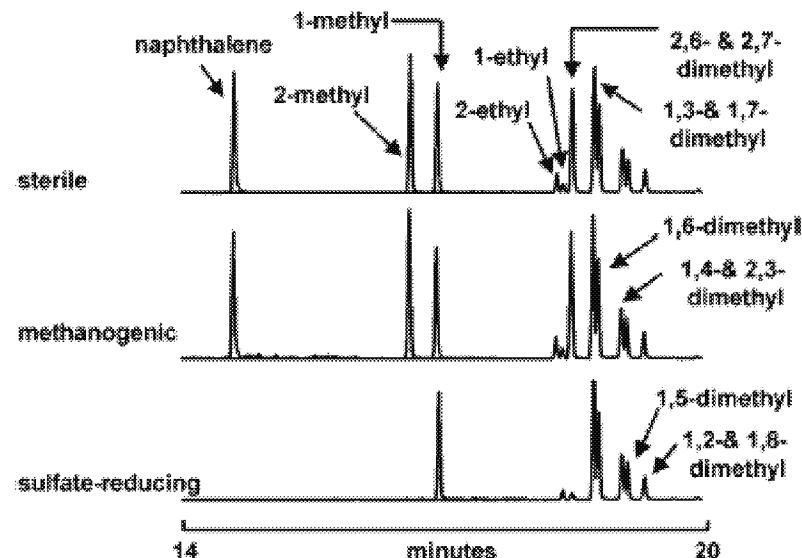


FIGURE 5. Selective biodegradation of naphthalene, 2-methylnaphthalene, 2-ethylnaphthalene, and the coeluting 2,6- and 2,7-dimethylnaphthalenes in Alba crude oil-amended incubations held under sulfate reducing conditions after 14 months. The m/z 128, 142, and 156 chromatograms are overlain.

PAH in Sediments

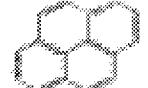
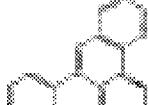
TABLE 1. Incremental Decline (over 11 Months) of in Situ PAHs in Microcosms of Anoxic, Coal Tar-Contaminated Boston Harbor Sediment Maintained with Adequate Sulfate To Support Respiration in Sulfate-Reducing Bacteria

| | Initial PAH level (nmol/Kg dry sediment) | PAH levels and % decline over ca. 1 yr (μ mol PAH / Kg dry sediment) | | | |
|------------------------|---|--|-----------------|----------------|----------------|
| | | after 105 days | after 220 days | after 338 days | |
| Naphthalene | | 436 ± 29 | 398 ± 24 8% | 399 ± 16 8% | 342 ± 2 22% |
| → 1-methyl-naphthalene | | 54 ± 11 | 30 ± 6 45% | 26 ± 1 52% | 22 ± 1 60% |
| → 2-methyl-naphthalene | | 99 ± 10 | 77 ± 6 22% | 73 ± 2 26% | 61 ± 3 38% |
| → Acenaphthene | | 132 ± 14 | 35 ± 2 74% | 19 ± 2 86% | 15 ± 1 89% |
| → Fluorene | | 112 ± 19 | 51 ± 5 54% | 43 ± 1 61% | 36 ± 0 67% |
| → Phenanthrene | | 231 ± 30 | 131 ± 13 43% | 110 ± 4 53% | 97 ± 3 58% |
| → Anthracene | | 293 ± 55 | 269 ± 16 8% | 153 ± 9 48% | 97 ± 6 67% |

PAH in Sediments



More complex PAH relatively difficult to degrade

| Fluoranthene |  | 970 ± 70 | 986 ± 69 0% | 900 ± 36 7% | 850 ± 47 12% |
|-----------------------|---|-------------|------------------|-----------------|-----------------|
| Pyrene |  | 1,015 ± 112 | 1,097 ± 70 0% | 964 ± 29 5% | 885 ± 20 13% |
| Benz[a]-anthracene |  | 301 ± 63 | 325 ± 23 0% | 293 ± 12 2% | 273 ± 9 9% |
| Chrysene |  | 385 ± 41 | 389 ± 27 0% | 329 ± 11 15% | 288 ± 1 25% |
| Benzo[b]-fluoranthene |  | 258 ± 19 | 260 ± 19 0% | 231 ± 10 11% | 218 ± 9 16% |
| Benzo[k]-fluoranthene |  | 203 ± 17 | 206 ± 10 0% | 191 ± 19 5% | 177 ± 6 13% |
| Benzo[a]pyrene |  | 330 ± 27 | 302 ± 22 8% | 258 ± 10 22% | 250 ± 6 24% |

PAH in Sediments

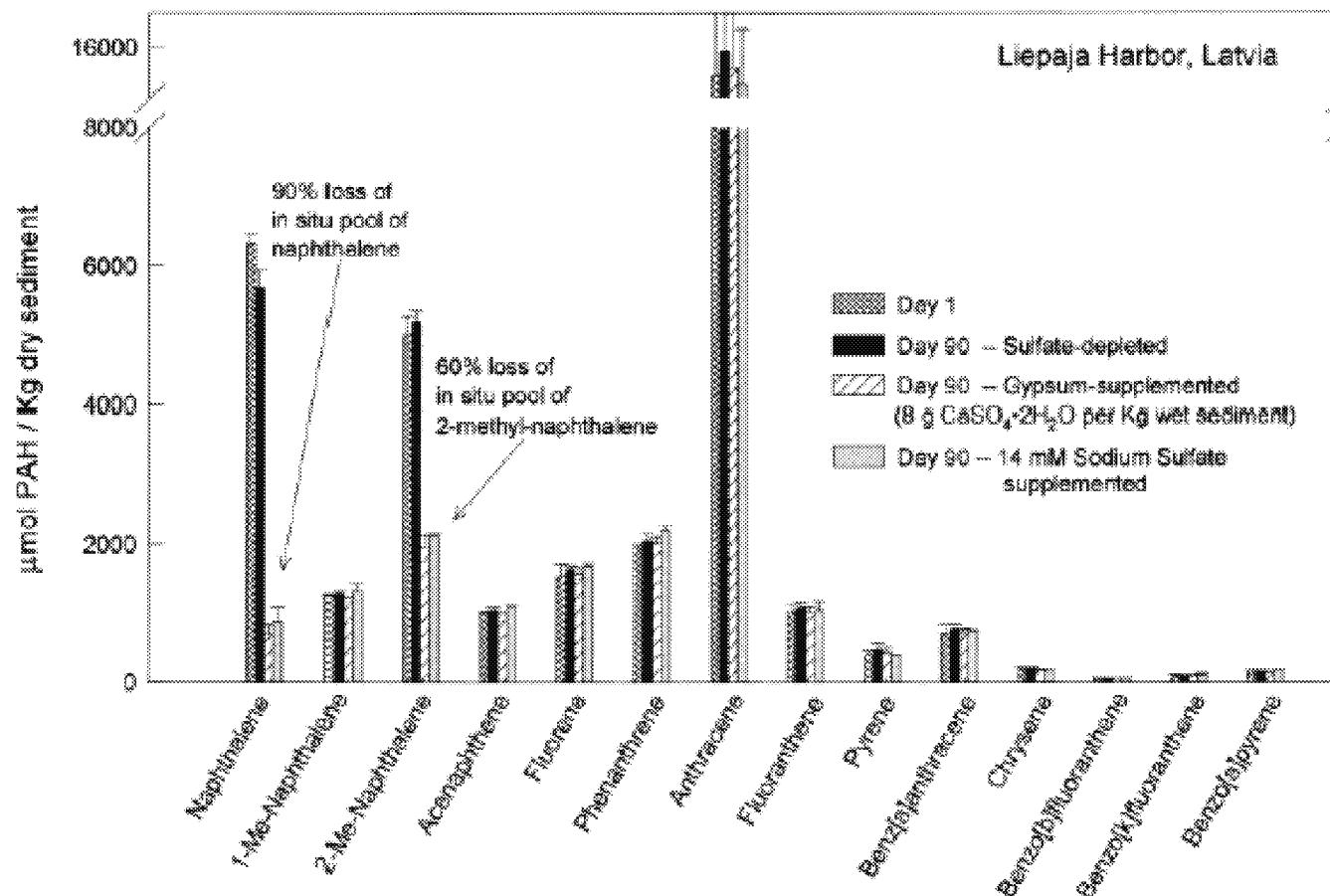


FIGURE 3. In situ contaminant PAHs in sediment approximately 3 weeks after collection from Liepaja Harbor, Latvia and after 90 days of incubation under in situ-like conditions. The sediment was sulfate-depleted upon arrival in the laboratory. Gypsum-supplemented and sodium sulfate-supplemented samples were amended after sediment was placed in incubation bottles. The results are the means of duplicate sample bottles. Each bottle value was determined from triplicate extractions.

Anaerobic Benzene Biodegradation



Table 2. Summary of anaerobic benzene degradation that was published with different TEAP.

| TEAP conditions | Percentage degraded | Concentration (mM) | Originated from | Lag phase (d) | Reference |
|---|-----------------------------------|--------------------|--|---------------|-----------|
| CH ₄ /CO ₂ | 6 ¹ (50 ²) | 1.5 - 30 | Ferulic acid degrading sludge | 16 | (10) |
| CH ₄ /CO ₂ | 82 ¹ | 0.05 | aquifer sediment, MI | 420 | (12) |
| CH ₄ /CO ₂ | 73 ² | 0.675 | aquifer sediment, MI | 360 | (12) |
| CH ₄ /CO ₂ | 53 ¹ | ??? | aquifer Ponca City, OK | 0 | (28) |
| SO ₄ ²⁻ /H ₂ S | 90 ¹ | 0.20 | Seal Beach, CA | 70-100 | (9) |
| SO ₄ ²⁻ /H ₂ S | 92 ¹ | 1.7 | San Diego Bay, CA | 55 | (14) |
| SO ₄ ²⁻ /H ₂ S | 92 ³ | 0.125 | Guaymas Basin, Mexico | 84 | (18) |
| SO ₄ ²⁻ /H ₂ S | 78 ¹ | 0.050 | aquifer sediment, MI | 400 | (12) |
| SO ₄ ²⁻ /H ₂ S | 76 ¹ | 0.057 | Seal Beach, CA | 120 | (12) |
| SO ₄ ²⁻ /H ₂ S | 85 ² | 0.125 | NY/NJ Harbor sediment | 60 | (12) |
| SO ₄ ²⁻ /H ₂ S | 101 ² | 0.100 | Sleeping Bear Dunes National Lakeshore, Empire, MI | 100 | (20) |
| NO ₃ /N ₂ | 95 ⁴ | 0.038 | Canada Force Base Borden, Ontario | - | (17) |
| NO ₃ /NO ₂ | 92-95 ¹ | 0.150 | Toronto, Ontario | 30 | (3) |
| NO ₃ /NO ₂ | 92-95 ¹ | 0.150 | Fresh water swamp, Perth, Ontario | 30 | (3) |
| NO ₃ /N ₂ | 47 ¹ | 0.163 | Strain JJ and RCB | 0 | (7) |
| Fe ³⁺ /Fe ²⁺ | 86 ¹ 97 ² | 0.608 | Sediment Defense Fuel Center, Hanahan, SC | 87-122 | (16) |
| Fe ³⁺ /Fe ²⁺ | 95 ⁵ | 0.010 | Sediment Defense Fuel Center, Hanahan, SC | 25 | (15) |
| Fe ³⁺ /Fe ²⁺ | 46 ⁴ | 0.125 | NY/NJ Harbor sediment | 100 | (12) |
| Fe ³⁺ /Fe ²⁺ | 100 ⁴ | 0.003 | Potomac River, Maryland | 50 | (12) |
| Fe ³⁺ /Fe ²⁺ | 50 ¹ | ??? | USGS Groundwater Toxic site, Bemidji, MN | 0 | (1) |
| Fe ³⁺ /Fe ²⁺ | 90 ¹ | 0.050 | aquifer Ponca City, OK | ??? | (5) |

Naval Weapons Station, Seal Beach, CA

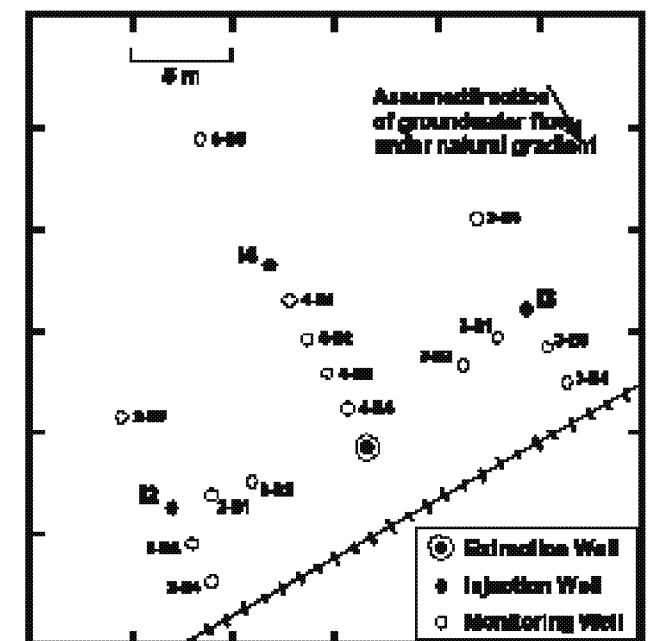
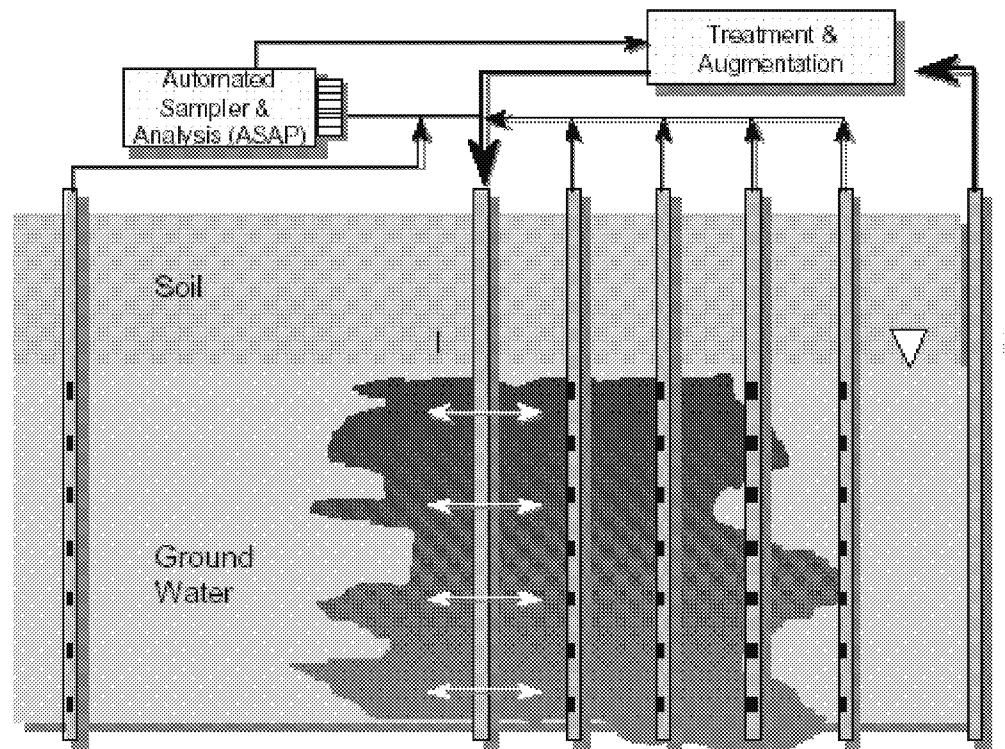


- Pilot study – Stanford University and NFESC
- “Injection-extraction” cells to create 3 remediation zones
 - With sulfate
 - With sulfate and nitrate
 - No amendment (naturally methanogenic)
- Sulfate and nitrate were quickly consumed → supply of electron acceptors was limiting under natural conditions
 - Nitrate (0.1 to 0.6 d^{-1}) and sulfate (0.1 d^{-1}) were consumed at similar rates
 - Nitrate effective at oxidizing sulfide back to sulfate
- BTEX removal:
 - Toluene preferentially degraded naturally over B, EB and X
 - Sulfate preferentially stimulated removal of o-X, but not B, EB and m+p-X
 - Nitrate stimulated removal of EB and m+p-X
 - Benzene biodegradation was the slowest in all conditions, if at all

ESTCP Cost & Performance Report, December 1999
<http://www.estcp.org/documents/techdocs/199522.pdf>

Application

Treatment and Augmentation System



ESTCP Cost & Performance Report, December 1999
<http://www.estcp.org/documents/techdocs/199522.pdf>

BTEX Removal with Sulfate and Nitrate

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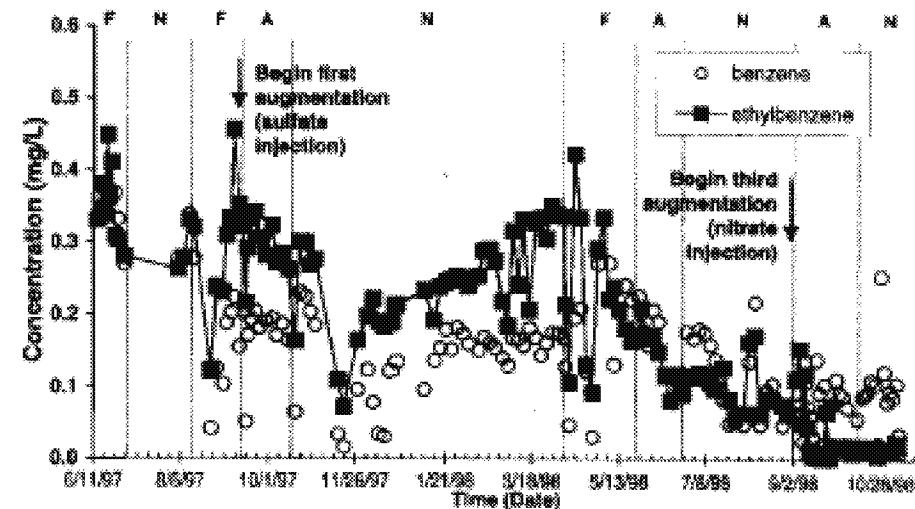
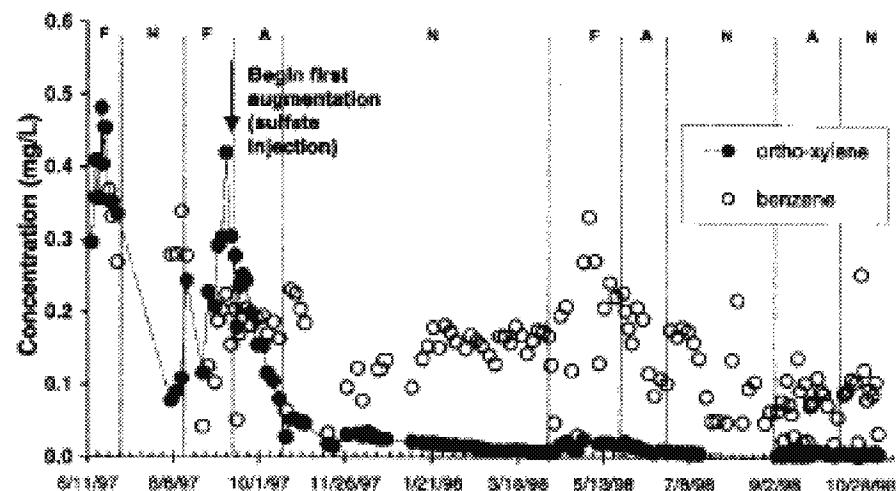


Figure 11. Concentration histories of benzene, *o*-xylene, and ethylbenzene at well 2-B1-4. Upper graph: augmentation with sulfate preferentially stimulates removal of *o*-xylene. Lower graph: ethylbenzene is recalcitrant under sulfate-reducing conditions, but is readily removed under nitrate-reducing conditions.

MTBE – Surface Water Sediments



TABLE 1. Final Percentage Distribution of ^{14}C Radioactivity in Surface Water–Sediment Microcosms after 166 Days^a

| sediment | amendment | experimental | | | | control |
|-------------------|-----------------|--------------------|--------------------|-------------------------|------------------------|------------------------------------|
| | | $^{14}\text{CH}_4$ | $^{14}\text{CO}_2$ | [^{14}C]MTBE | [^{14}C]TBA | ^{14}C total ^b |
| Cecil Field | O ₂ | nd ^d | 90 ± 12 | 8 ± 7 | nd | 98 ± 8 |
| | NO ₃ | nd | 75 ± 14 | 29 ± 2 | nd | 104 ± 12 |
| | Mn(IV) | 2 ± 3 | nd | 92 ± 5 | 7 ± 1 | 101 ± 3 |
| | Fe(III) | 3 ± 2 | nd | 88 ± 3 | 9 ± 1 | 100 ± 3 |
| | SO ₄ | nd | 20 ± 4 | 82 ± 3 | 1 ± 1 | 103 ± 4 |
| | UA ^e | 3 ± 3 | nd | 94 ± 6 | 8 ± 1 | 105 ± 4 |
| Oasis | O ₂ | nd | 72 ± 12 | 35 ± 6 | nd | 107 ± 12 |
| | NO ₃ | nd | 33 ± 8 | 72 ± 1 | nd | 105 ± 7 |
| | Mn(IV) | 2 ± 1 | 6 ± 5 | 88 ± 7 | 6 ± 2 | 102 ± 6 |
| | Fe(III) | 3 ± 2 | nd | 92 ± 12 | 8 ± 4 | 102 ± 10 |
| | SO ₄ | nd | 9 ± 3 | 81 ± 9 | 9 ± 7 | 99 ± 7 |
| | UA ^e | 3 ± 2 | 2 ± 2 | 87 ± 10 | 11 ± 1 | 103 ± 8 |
| Picatinny Arsenal | O ₂ | nd | 58 ± 23 | 40 ± 3 | nd | 98 ± 21 |
| | NO ₃ | nd | 23 ± 5 | 81 ± 2 | nd | 104 ± 4 |
| | Mn(IV) | nd | 11 ± 2 | 90 ± 5 | 3 ± 2 | 104 ± 4 |
| | Fe(III) | nd | 14 ± 4 | 81 ± 10 | 4 ± 1 | 99 ± 10 |
| | SO ₄ | nd | 12 ± 3 | 82 ± 3 | 3 ± 0 | 97 ± 2 |
| | UA ^e | 4 ± 2 | nd | 89 ± 3 | 8 ± 1 | 101 ± 2 |

^a For each treatment, experimental data are means ± SD for triplicate microcosms, and control data are from a single microcosm. Radiolabeled C1–C4 organic acids were monitored but not detected in this study (MDL was 2%). ^b Total ^{14}C recovery as $^{14}\text{CH}_4$, $^{14}\text{CO}_2$, [^{14}C]MTBE, and [^{14}C]TBA in experimental microcosms. ^c Only [^{14}C]MTBE and [^{14}C]TBA were detected in control microcosms. The ratio of [^{14}C]MTBE:[^{14}C]TBA was 19:1 and did not differ significantly between treatments. ^d Not detected. The MDLs were 2%, 2%, and 1% for $^{14}\text{CH}_4$, $^{14}\text{CO}_2$, and [^{14}C]TBA, respectively.

^e Unamended treatment. For all sediments, unamended treatments were methanogenic.

TBA accumulation tendency increased with more anaerobic conditions

MTBE – Marine Sediment Enrichments with Sulfate

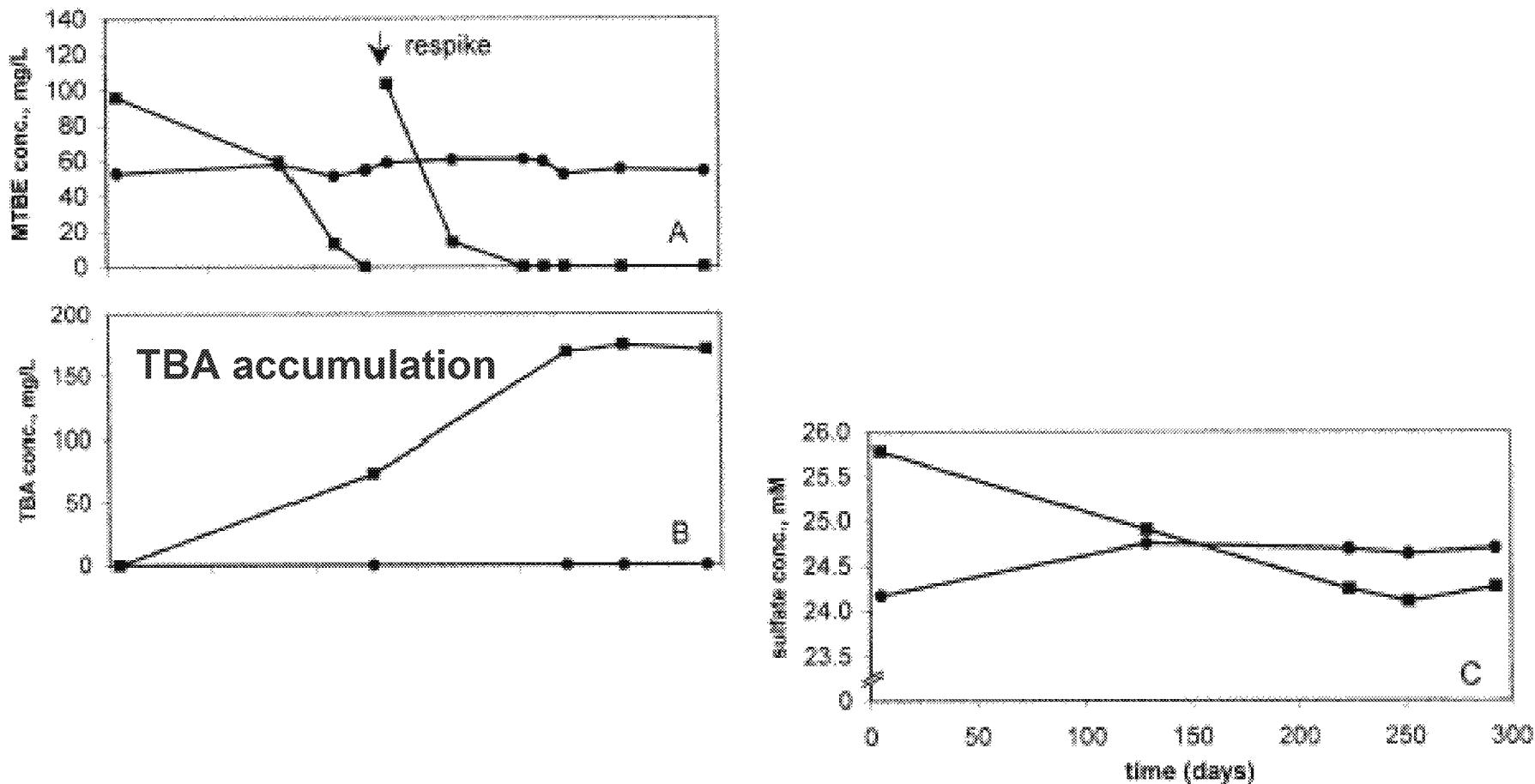


Fig. 2. Anaerobic biotransformation of MTBE by MTBE-enriched sulfidogenic cultures (■) upon transfer into fresh sulfidogenic medium, compared to those of sterile control (●). MTBE biotransformation (A), TBA formation (B), sulfate reduction(C).

Somsamak, P. et al., FEMS Microbiol. Ecology., 37, 259-264, 2001²²

TBA – Surface Water Sediments



TABLE 1. Final Distribution of ^{14}C Radioactivity in Surface-Water Sediment Microcosms after 198 Days^a

| sediment | amendment | experimental | | | control ^{14}C -total ^b |
|------------|-----------------|--------------------|---------------------|-------------------------|--|
| | | $^{14}\text{CO}_2$ | $^{14}\text{C-TBA}$ | $^{14}\text{C-total}^b$ | |
| Laurens | O ₂ | 99 ± 2 | ND ^d | 99 ± 2 | 91 |
| | NO ₃ | 70 ± 10 | 20 ± 18 | 90 ± 18 | 95 |
| | Mn(IV) | 75 ± 20 | 14 ± 10 | 89 ± 10 | 95 |
| | Fe(III) | ND | 97 ± 13 | 97 ± 13 | 107 |
| | SO ₄ | 5 ± 1 | 92 ± 6 | 97 ± 4 | 96 |
| | UA ^e | ND | 100 ± 3 | 100 ± 3 | 103 |
| Charleston | O ₂ | 99 ± 3 | ND | 99 ± 3 | 104 |
| | NO ₃ | 28 ± 5 | 66 ± 6 | 94 ± 4 | 95 |
| | Mn(IV) | ND | 94 ± 8 | 94 ± 8 | 91 |
| | Fe(III) | ND | 101 ± 2 | 101 ± 2 | 96 |
| | SO ₄ | 4 ± 1 | 92 ± 4 | 96 ± 3 | 96 |
| | UA | ND | 100 ± 0 | 100 ± 0 | 108 |

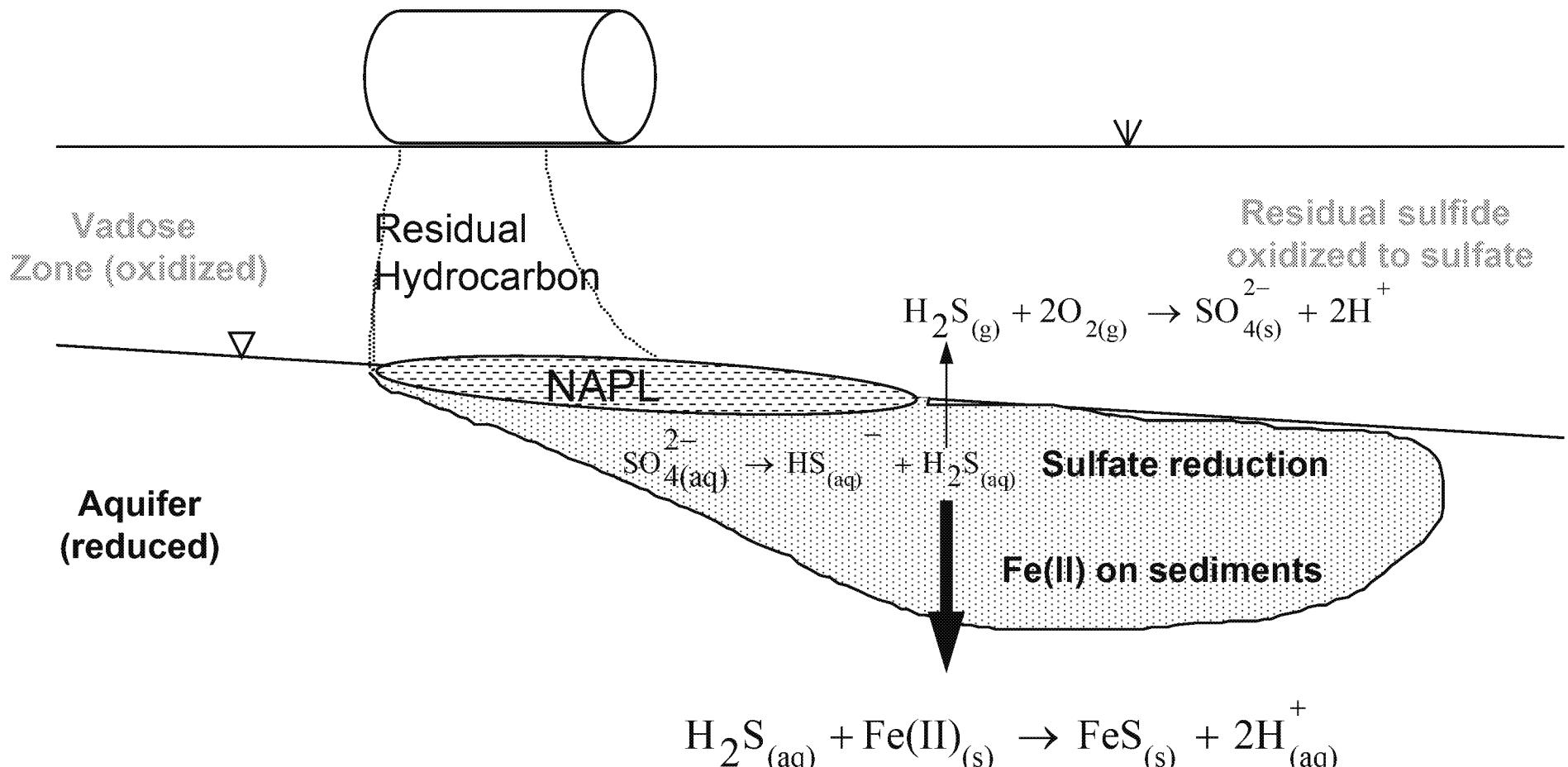
^a Recoveries are given as the percentage of radioactivity initially added to the sediment microcosms as $^{14}\text{C-TBA}$. Experimental data for each treatment are means ± SD for triplicate microcosms and control data are from a single microcosm. Radiolabeled C1–C4 organic acids were monitored but not detected in this study (MDL was 2%). ^b Total ^{14}C recovery as $^{14}\text{CO}_2$ and $^{14}\text{C-TBA}$ in experimental microcosms. ^c Only $^{14}\text{C-TBA}$ was detected in control microcosms. ^d Not detected. The MDLs were 2% and 1% for $^{14}\text{CO}_2$ and $^{14}\text{C-TBA}$, respectively. ^e Unamended treatment. For both sediments, unamended treatments were methanogenic.

What About Hydrogen Sulfide?



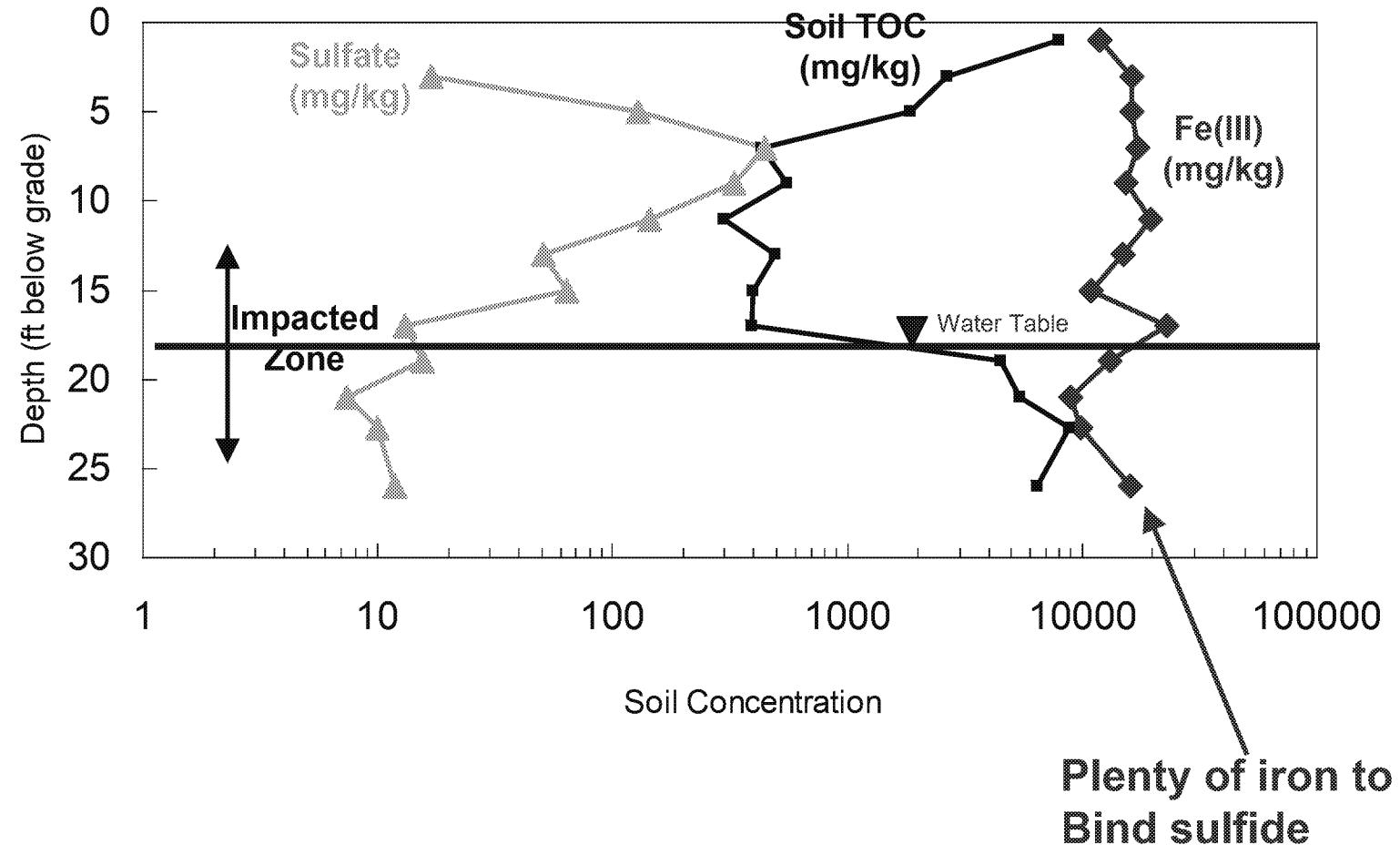
- Colorless gas with a strong odor of rotten eggs
- Exposure limits
 - NIOSH: 10 ppmv (10 minutes)
 - OSHA: 20 ppmv
 - IDLH: 100 ppmv
- Health Hazards
 - Inhalation: irritation to eyes, conjunctivitis, affects CNS
 - Ingestion: excitement, colored urine
 - Contact: nausea, dizziness, suffocation, rapid breath
- Explosive limits: 4% to 44%

Most of Sulfide is Bound to Soil



Sulfide sequestered as iron sulfides $\text{FeS} + \text{S}^0 \rightarrow \text{Fe}_2\text{S}$

Soil Profile at Neodesha (SOW-9)



Refinery Site in Oklahoma

- Operating refinery with an old benzene plume (max. 7.8 mg/L)
- Hydrogeology:
 - Coarse sand (GW seepage velocity 2500 ft/y)
 - DTW: 9-12 ft bgs
- Sodium sulfate injection
 - 40 one-inch wells in 2 rows
 - Sulfate injected: 770 mg/L @ 0.14 gpm (total flow)
 - Maximum sulfate detected in GW: 58 mg/L
 - Sulfide not detected in GW
- **Benzene concentrations were reduced between 73% to 93% in 165 days (half life ~ 2 months)**

Benzene Reduction Following Sulfate Addition

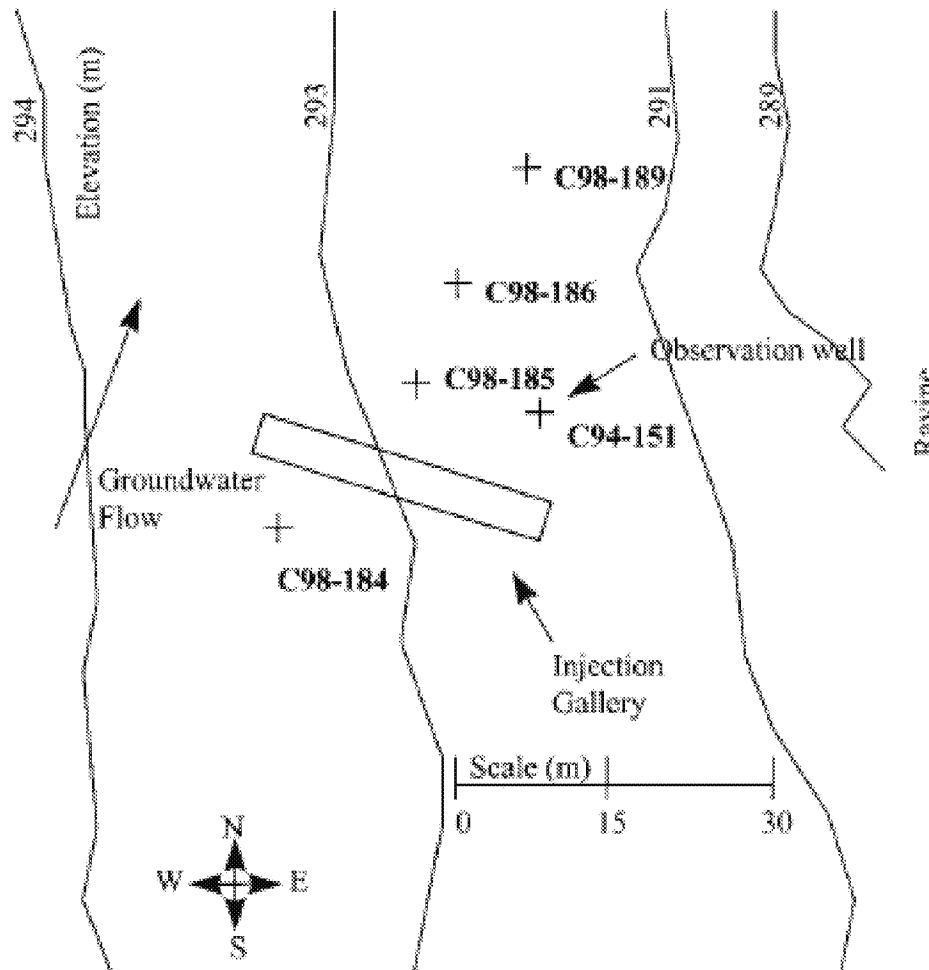


FIGURE 1. Plan view of the injection gallery and positions of the observation wells.

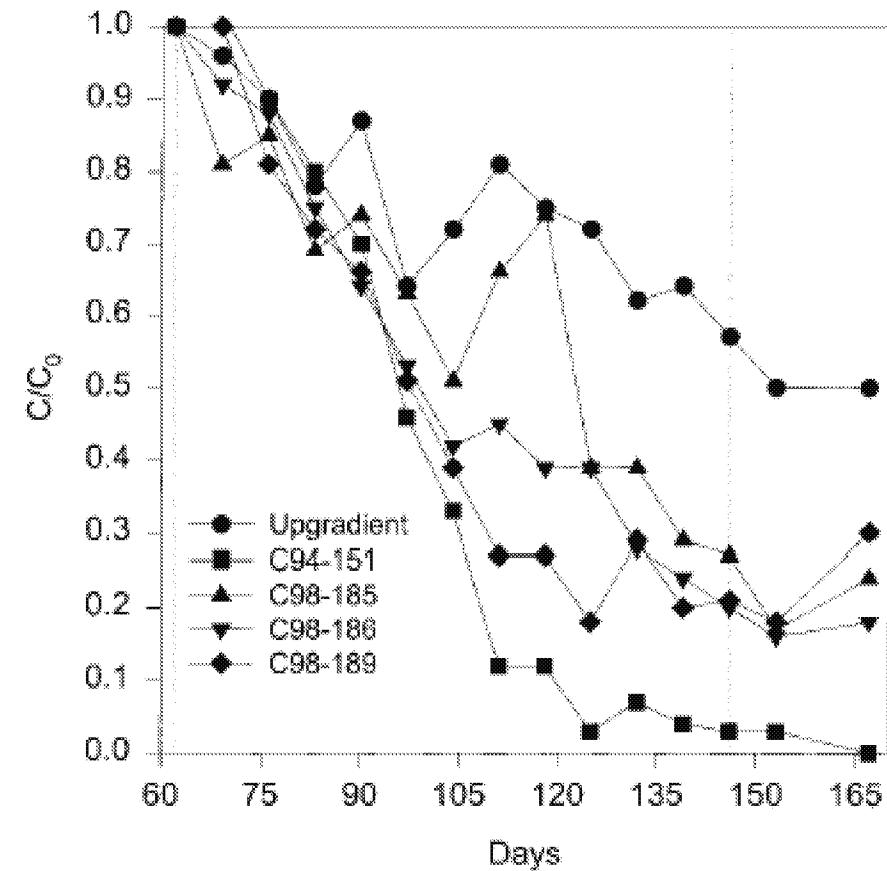
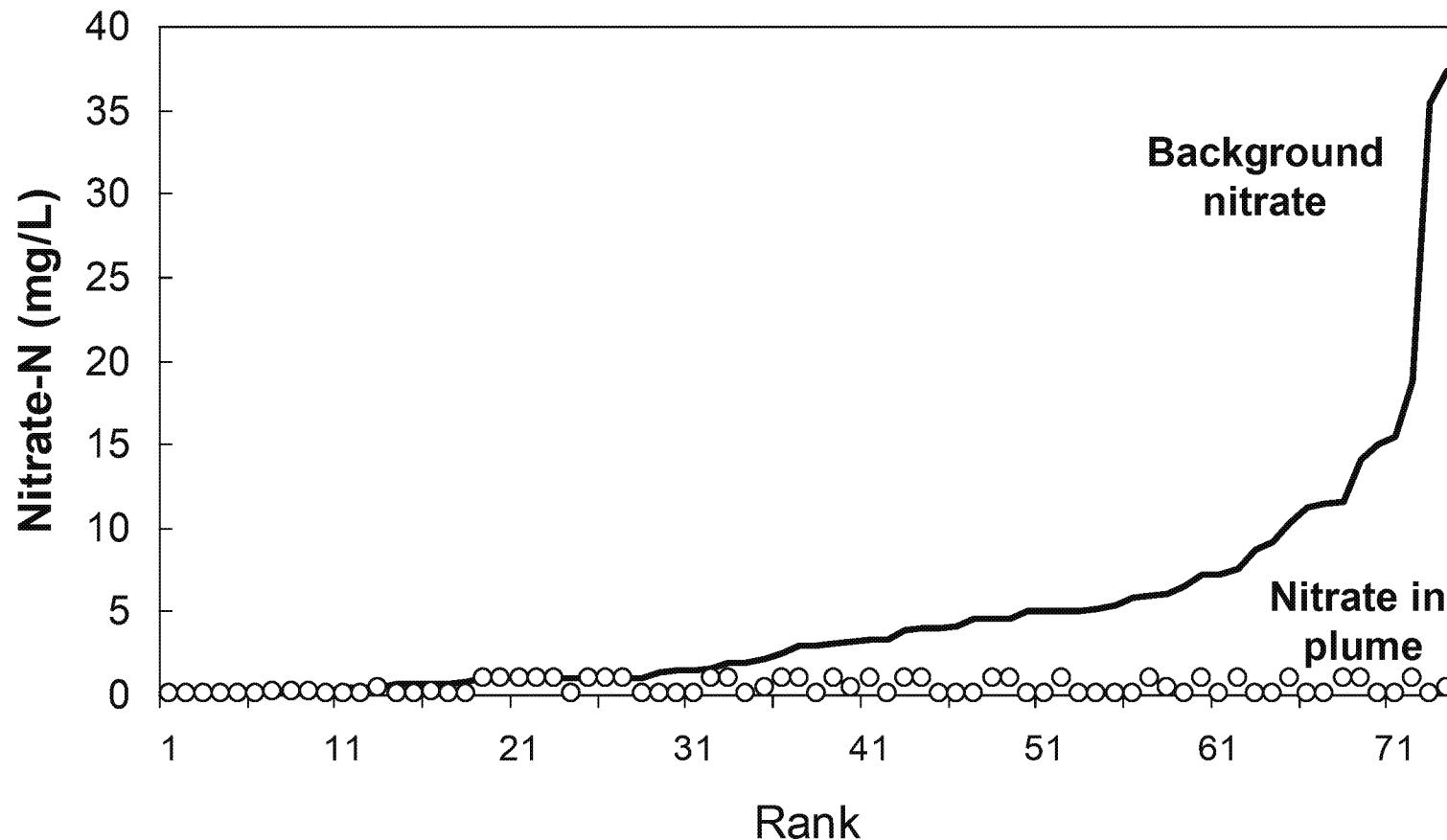


FIGURE 5. Relative decreases in benzene concentrations at the observation wells. All concentrations are normalized to observed benzene concentrations measured just prior to the start of the injection period. Dashed lines indicate the period of sulfate injection.

Anderson and Loveley, Enviro. Sci. Technol., 34, 2261-2266, 2000²⁸

Nitrate for Enhanced Bioremediation



**Background nitrate concentrations are generally lower
and nitrate is depleted in plumes**

Nitrate for Enhanced Bioremediation



Facts

- Background levels are generally low
- Primary MCL of 45 mg/L nitrate
- Like oxygen, nitrate is utilized to oxidize reduced species (e.g. iron sulfides), as well as other organic carbon

Observations from Field Studies in Literature

- ⇒ Most pilots and field applications have employed extraction-injection pairs (“recirculation cell”)
- ⇒ Injection concentrations – 50 – 200 mg/L nitrate
- ⇒ Monitoring periods from 2 to 5 months
- ⇒ Required 10 to 100 times more nitrate over that required for BTEX biodegradation. Nitrate known to oxidize sulfide back to sulfate.
- ⇒ TEX compounds degraded, but Benzene generally remained persistent (total duration too short?). Recent evidence of benzene biodegradation with nitrate.
- ⇒ Consider nitrate together with sulfate to increase the electron acceptor pool
 - ⇒ Naval weapons site, Seal Beach, CA data recommend the same

Benzene and Nitrate Reduction

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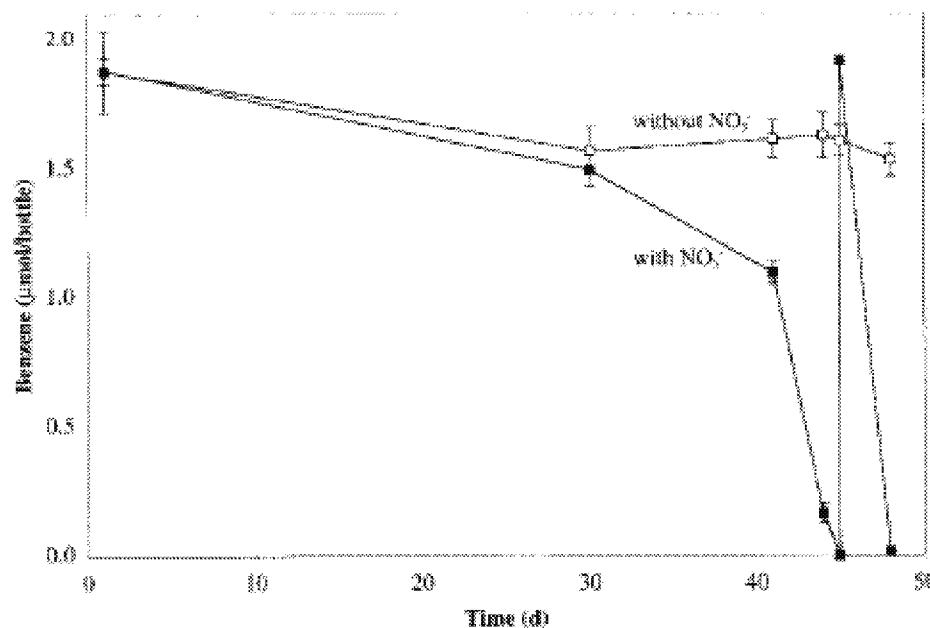


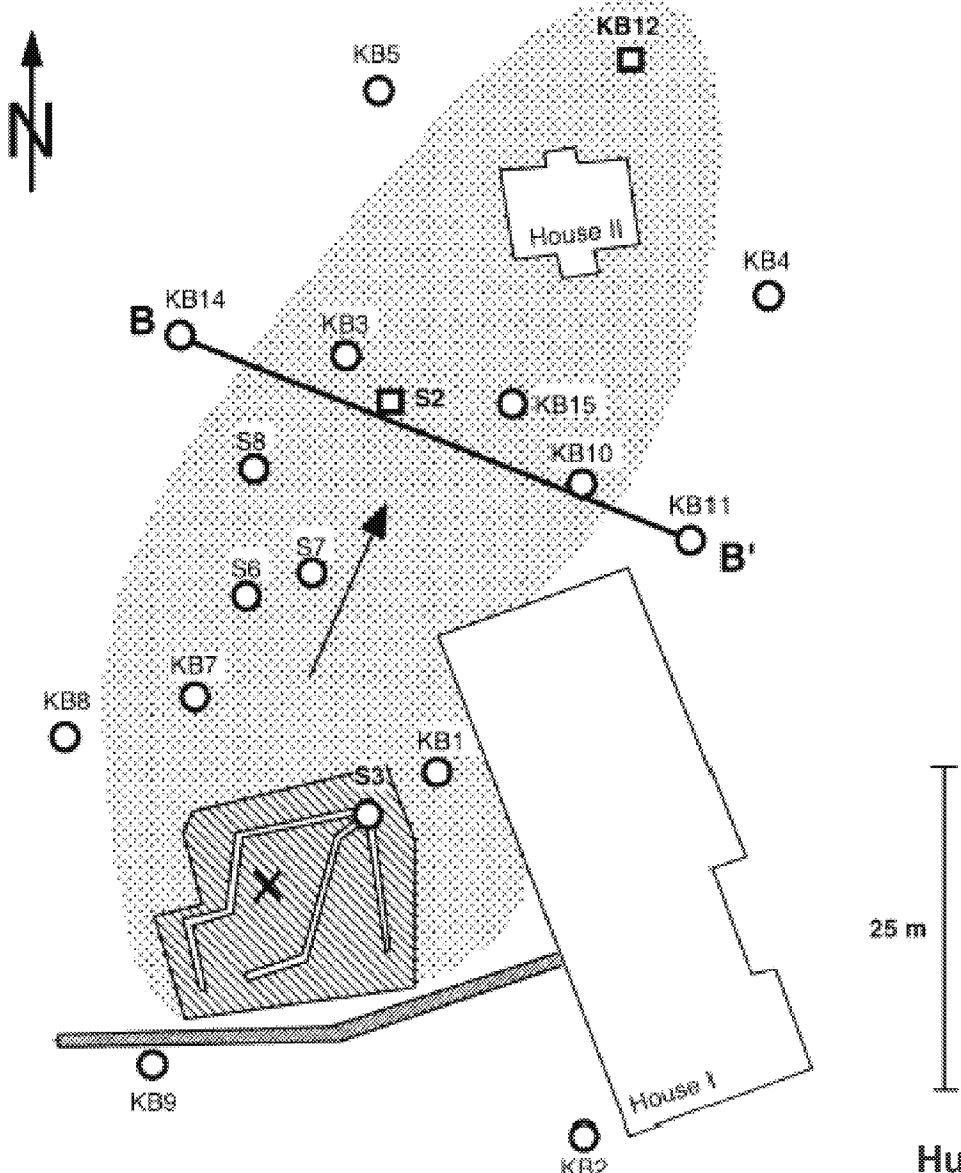
FIG. 2. Plot of benzene concentration versus time for transfer cult in the presence of nitrate (■) and in the absence of nitrate (□). Tl means \pm standard deviations from triplicate cultures (without n means \pm ranges from duplicate cultures (with nitrate). d, days.

TABLE 1. Benzene biodegradation in microcosms and enriched cultures

| Microcosms or cultures | Year(s) | Rate of benzene degradation ($\mu\text{mol/liter/day}$) | Nitrate/benzene ratio |
|------------------------------------|-----------|---|-----------------------|
| Original microcosms | 1995 | 3.2 (0.14) ^a | 49.6 (15.8) |
| Enriched microcosms | 1995–1997 | 7.6 (0.10) | 12.6 (3.3) |
| First-generation transfer cultures | 1997 | 11.0 (2.5) | 11.1 (2.5) |
| Subsequent transfer cultures | 1997–1998 | 18.7 (13.0) | 10.1 (1.7) |

^a Values are means (standard deviations). Rothermich et al., *Enviro. Sci. Technol.*, **36**, 4811–4817, 2002

Engineered Bioremediation of a Diesel-impacted Aquifer



- Menziken, Switzerland
- 4.5 years
- GW pumped from S2 or KB12
- Water aerated and amended with KNO₃ (84 mg/L nitrate) and ammonium phosphate
- Re-injected in S3 connected to infiltration gallery

Hunkeler et al., J. Contam. Hydro., 59, 231-245, 2002³²

Natural Diesel Biodegradation Following Engineered Bioremediation

gem
group environmental management

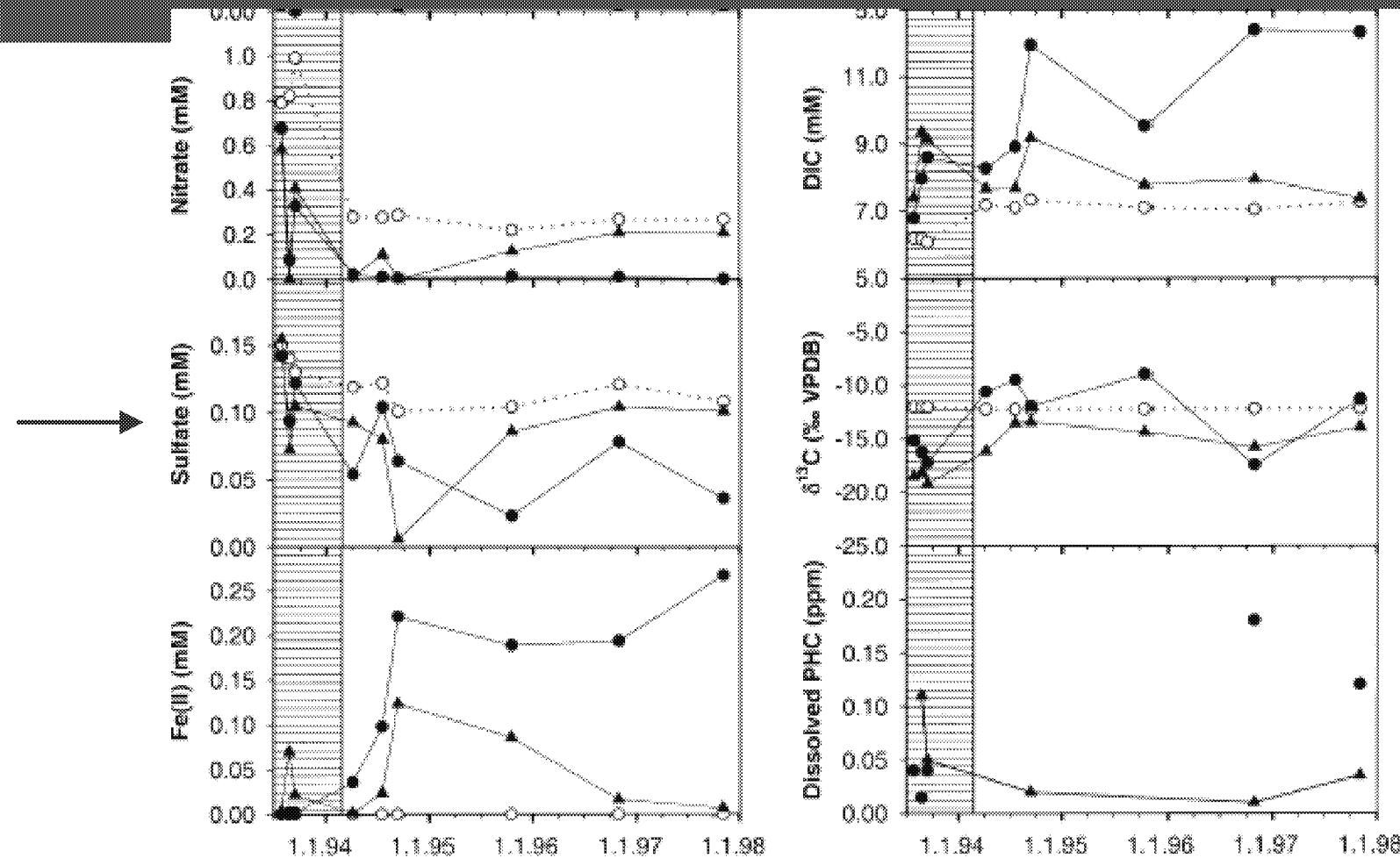


Fig. 3. Values of selected parameters for monitoring wells S6 (●) and KB15 (▲) during and after engineered in situ bioremediation. Expected values at S6 if the species entering the contaminated zone had behaved like a non-reactive tracer (○). The expected values were calculated according to Eq. (3). Shaded area: engineered in situ bioremediation in operation.

Hunkeler et al., J. Contam. Hydro., 59, 231-245, 2002³³

Applications



- Dissolved Plume
 - Addition of solution of sulfate salts (e.g. epsom, sodium sulfate)
 - Design sulfate addition (concentration and flow rate) based on sulfate demand for the mass flux of dissolved BTEX
 - Continuous addition, Periodic slug addition
 - Row of addition wells, infiltration gallery
 - Gypsum socks in transect of wells
 - Extract down-gradient, amend sulfate-nitrate and re-infiltrate up-gradient
- Source Area (or hotspots)
 - Agricultural gypsum amendment (up to 1% w/w) to source area excavation backfill material as a long term source of sulfate
 - Cost effective: ag gypsum ~ \$ 19 to 150/t vs \$16530/ton for ORC
 - Site selection criteria and application procedure (Gypsum FAQs)

Site Selection Criteria (Sulfate)



- Site with residual impact (“sheen” or high dissolved), but not with “gross” free product impacts
- Shallowest water table > 5 ft below grade
- Distance to residence, surface water or private well > 100 ft
- Distance to municipal DW well (100s of gpm) > 1250 ft
- Analyze GW samples from “clean” and “impacted” wells for BTEX, sulfate, sulfide, Fe(II), pH, Total Inorganic Carbon (or total alkalinity). Site suitable if
 1. Sulfate in clean wells > 15 mg/L and
 2. Sulfate depleted in impacted wells
 3. Elevated Fe(II) in impacted wells

Remedial Design Guidance



Data Input (in yellow highlighted cells)

| | | Comments/Basis |
|--|-------------|---|
| Site Name | | |
| Hydraulic Conductivity Estimate (K) | 200 ft/d | Preferably based on slug test or pump test data |
| Thickness of impacted saturated zone | 10 ft | Estimate as length of screened interval of most impacted well |
| Hydraulic gradient | 0.003 ft/ft | |
| Width of GW plume being addressed | 10 ft | Lateral extent of proposed treatment (e.g. row of wells) |
| Maximum BTEX concentration | 3.50 mg/L | |
| Safety Factor for sulfate demand (over stoichiometric) | 2 | Assume 2 to 4 |
| Injection Sulfate Concentration | 500 mg/L | Higher of sulfate in un-impacted water or 250 mg/L |
| Number of injection wells | 2 | Design choice |

Calculations

| | |
|---|-----------------------|
| Total groundwater volumetric flux (Q = KiA) | 60 ft ³ /d |
| Mass flux of BTEX Through Treatment Zone | 5945 mg BTEX/d |
| BTEX degraded/mass of sulfate | 0.22 (mg/mg) |
| Stoichiometric Sulfate Demand | 27025 mg sulfate/d |
| Total sulfate injection volume (w/ safety factor) | 29 gal/d |

Design Choices for Liquid Sulfate Addition

Option 1: Continuous Addition

| | | |
|--------------------|----------------|---|
| Solution Flow/well | 0.010 gpm/well | Adjust sulfate concentration to get reasonable flow |
|--------------------|----------------|---|

Option 2: Addition in Slugs

| | |
|-----------------------------|--------------|
| Slug Addition Frequency | 2 times/week |
| Required Slug Addition Rate | 200 gal/week |
| Slug volume/well/event | 50 gal |

Chemical Requirements

| Salt Used | MW (gm) | Quantity Required (gm/d) | Unit Cost (\$/lb) | Chemical Cost (\$/year) |
|-------------------------------------|------------|-----------------------------|----------------------|----------------------------|
| Epsom salt ($MgSO_4 \cdot 7H_2O$) | 120.37 | 68 | 0.75 | 41 |
| anhydrous Sodium Sulfate | 142 | 80 | 1.76 | 113 |

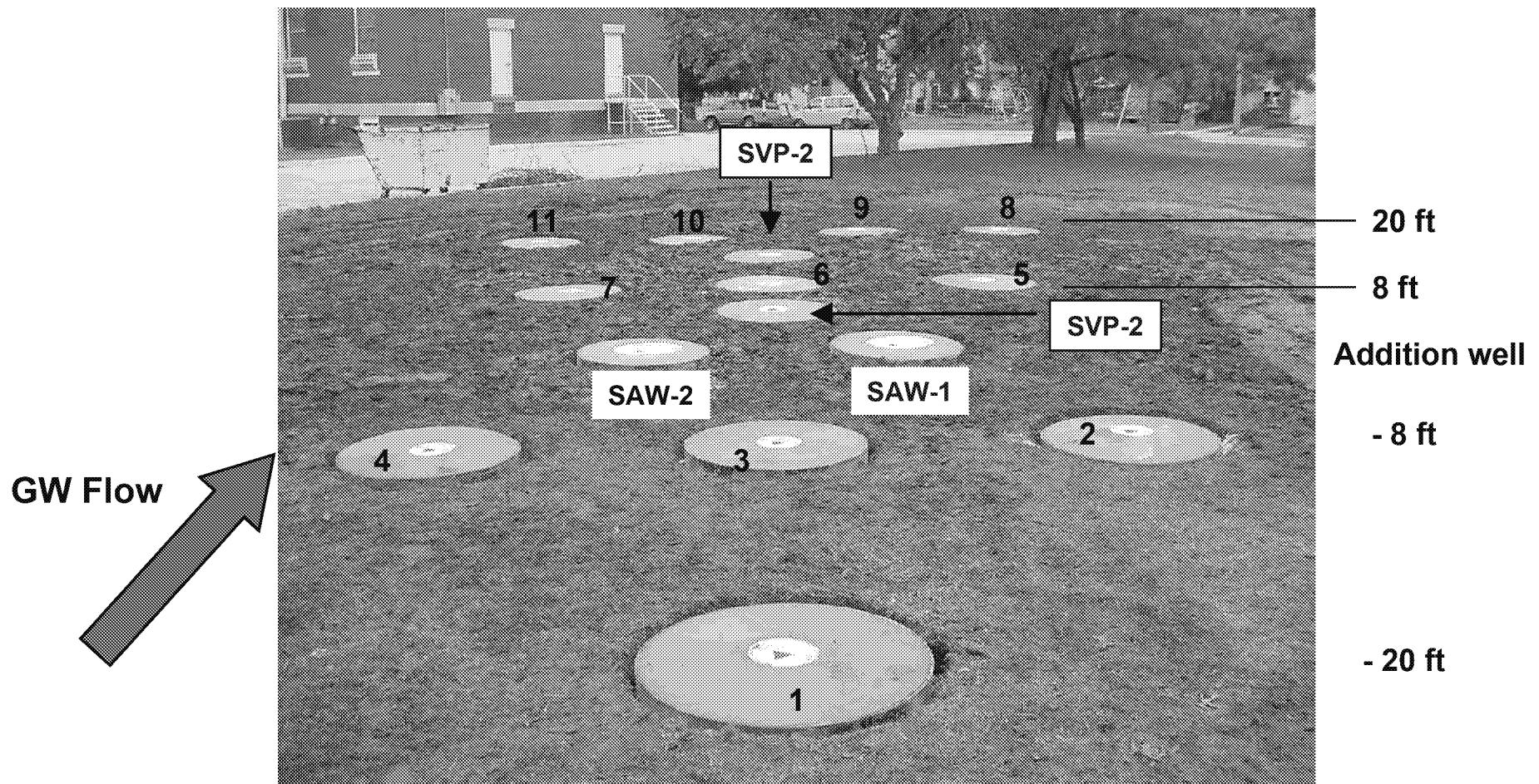
Summary

- Most plumes are anaerobic and depleted of soluble electron acceptors (nitrate and sulfate)
- Sulfate
 - Sulfate is more efficient and stimulates existing anaerobic conditions
 - Suitable for a variety of hydrocarbons – gasoline, gas condensate, alkanes, PAH, diesel...
 - Sulfide not been an issue in studies (OK refinery, Seal Beach site, other literature, closed BP refinery site)
 - Expect some lag time after sulfate shows up at the wells (3 – 6 months)!
- Nitrate
 - Useful to oxidize iron sulfides to sulfate
 - Useful to boost the total electron acceptor pool

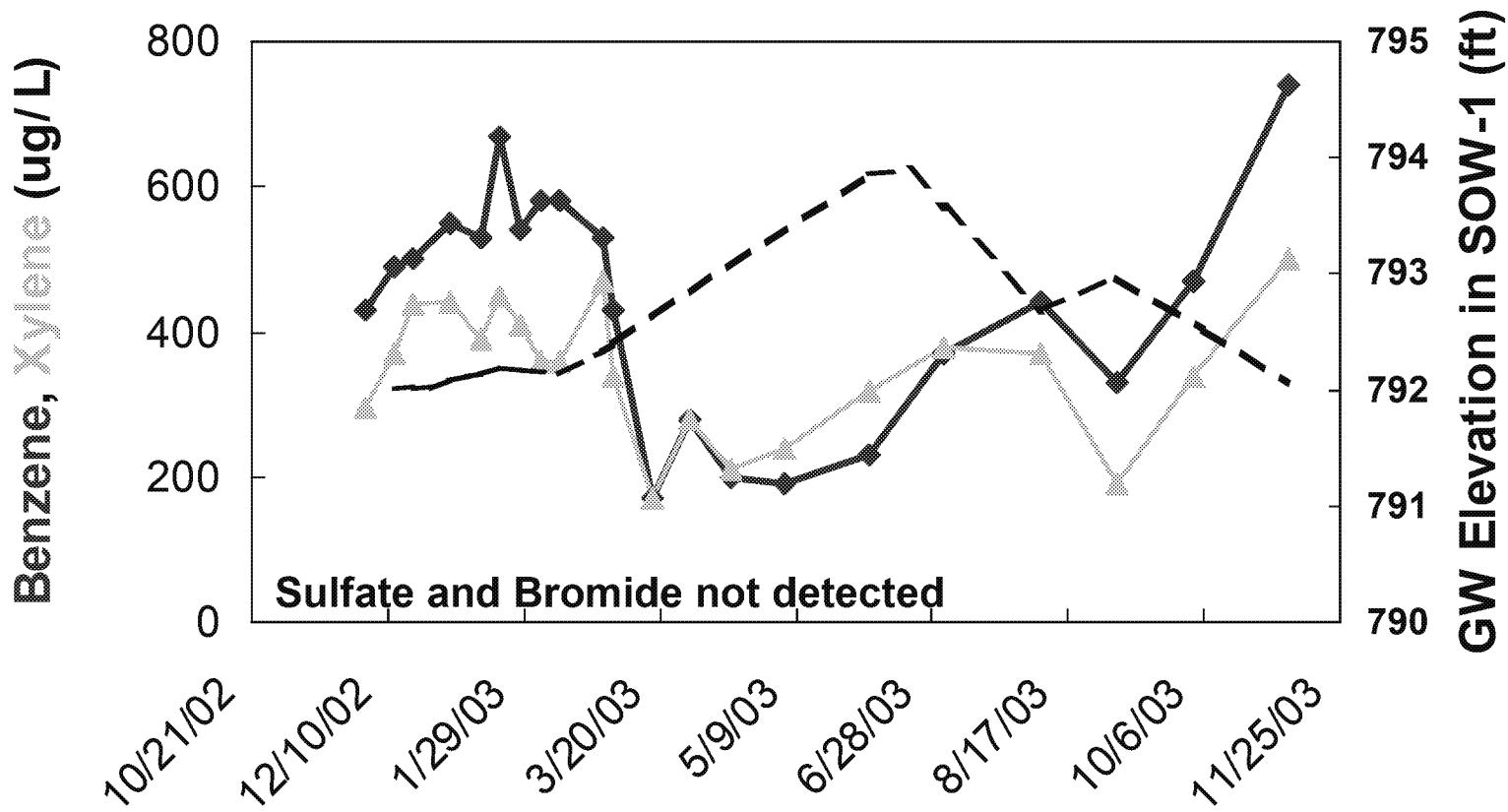


Pilot Layout

35 gal of 500 mg/L sulfate, 100 mg/L bromide twice a week/well

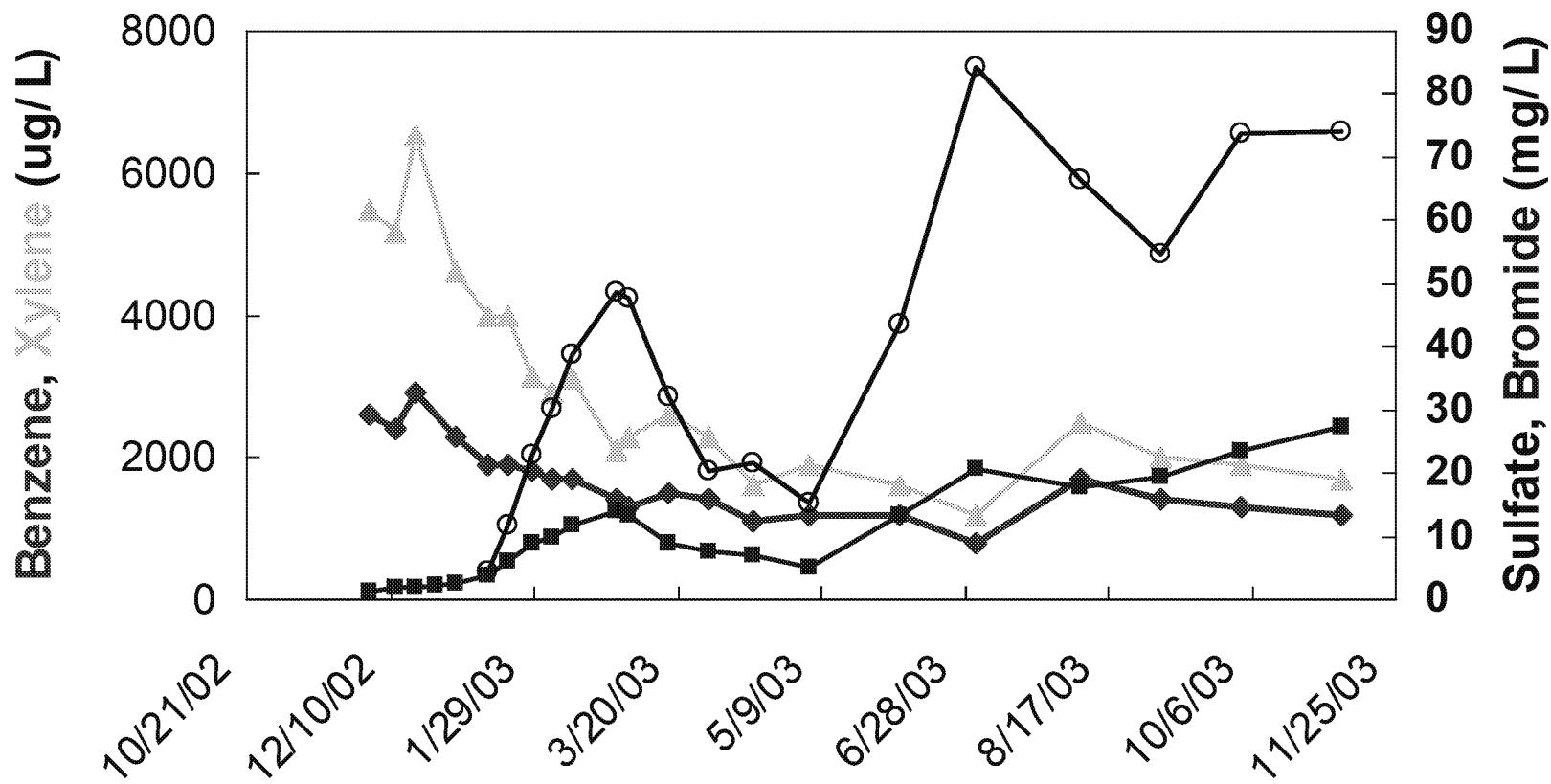


Up-gradient Well (SOW-1)



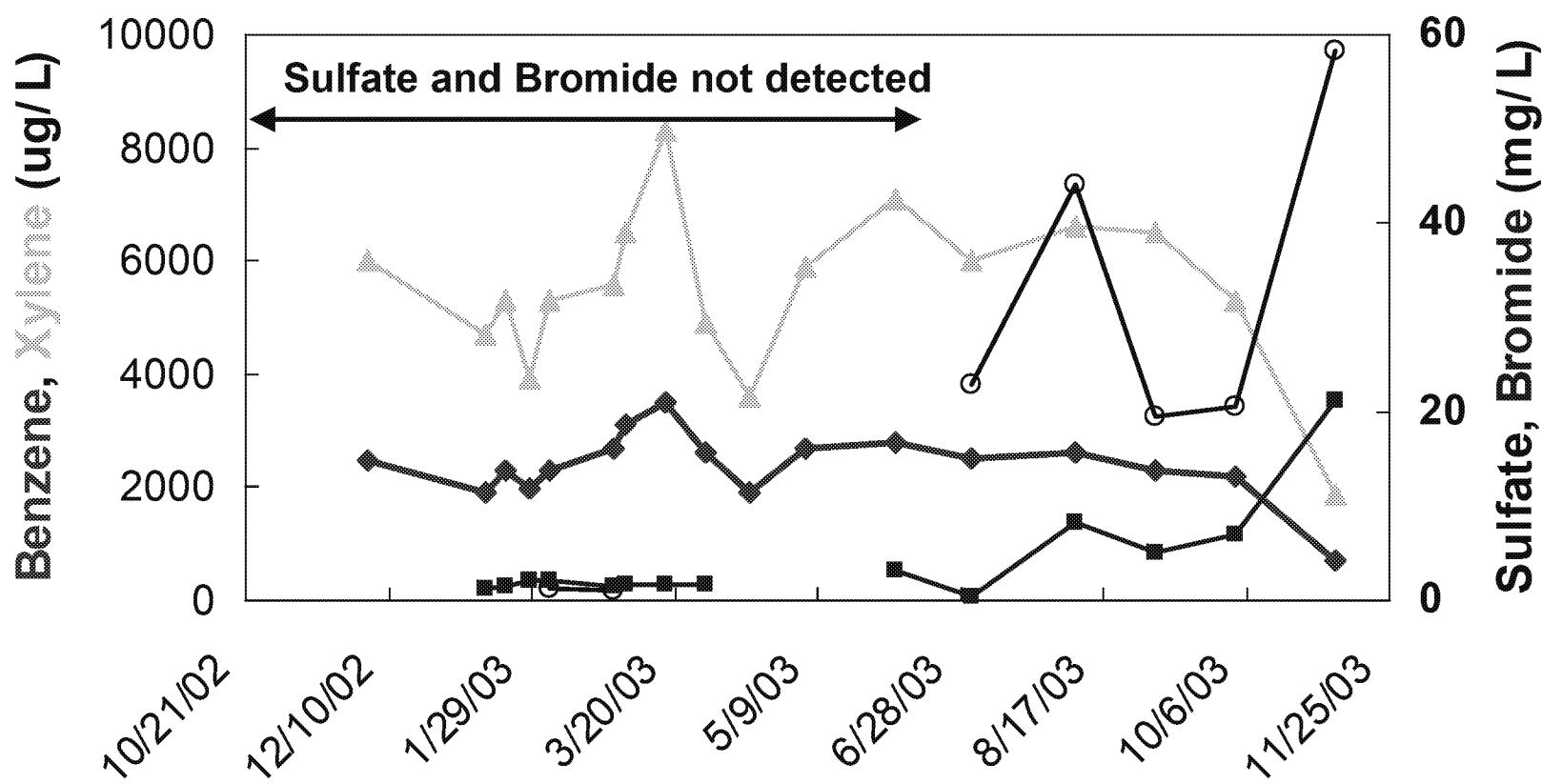
Variations in B and X related to groundwater fluctuations

20 ft Downgradient Well (SOW-10)



Significant decrease in B and X in presence of sulfate

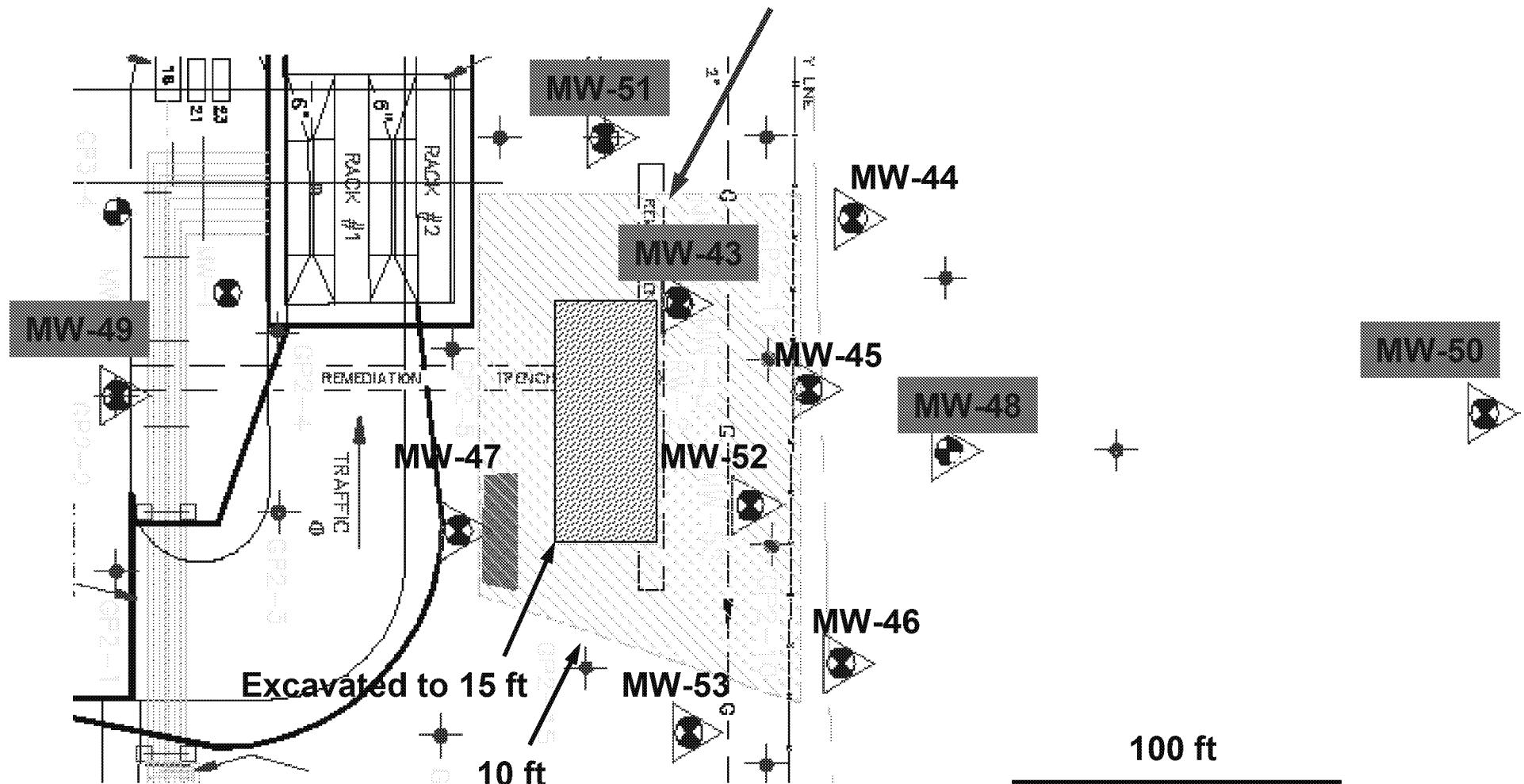
20 ft Downgradient Well (SOW-11)



Terminal in Minnesota Ag gypsum in Excavation



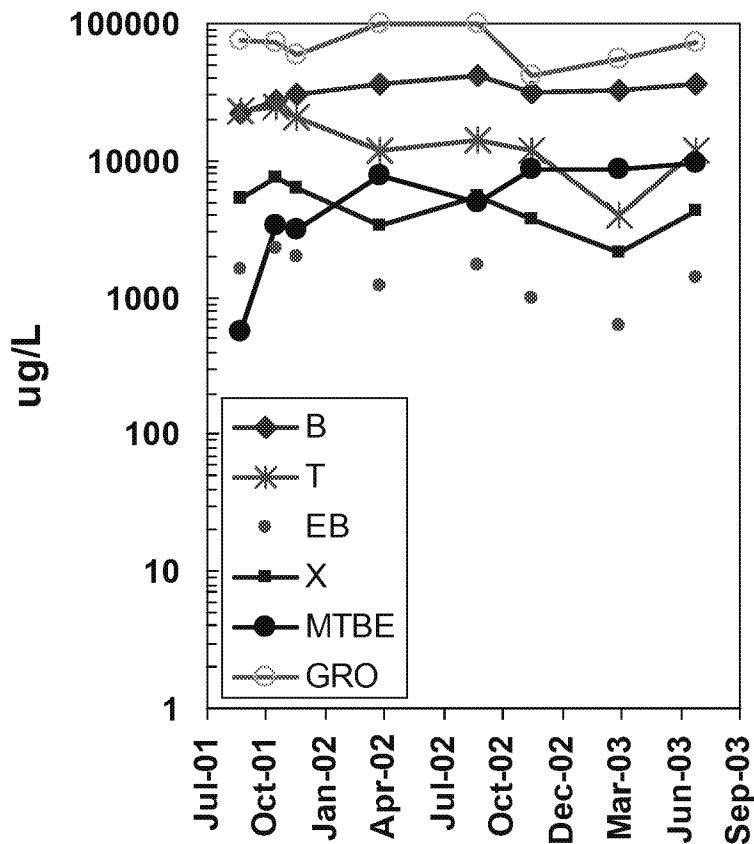
0.5% w/w ag gypsum in backfill



Effect of Sulfate on BTEX and TPH

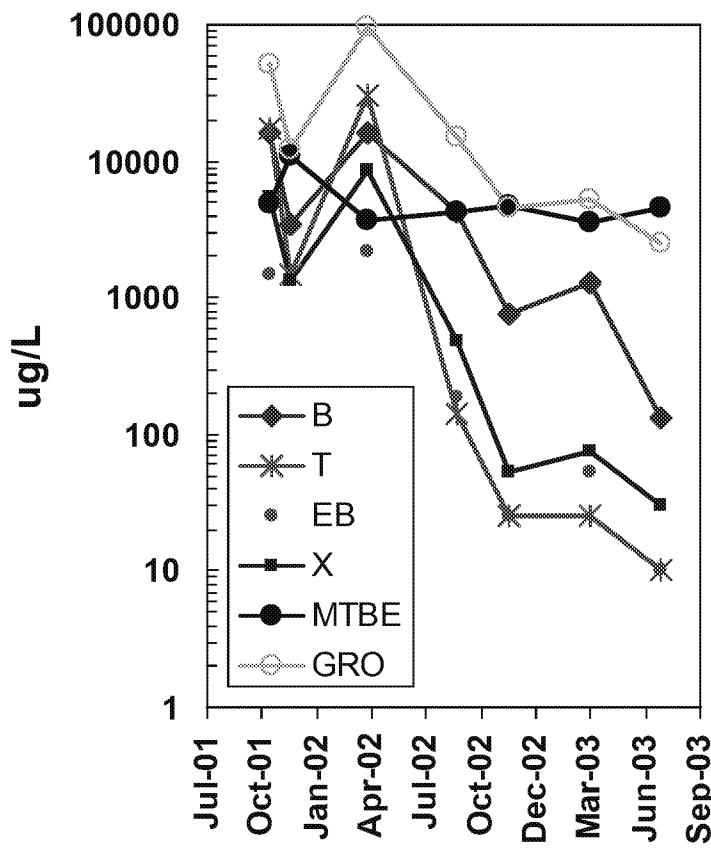


MW-49 Up-gradient of excavation



- Sulfate not present
- Groundwater impact stays

MW-45 Down-gradient of excavation



- Sulfate upto 290 mg/L
- Groundwater cleans up!